

σ versus π BONDING IN POLYMETHYLTHIOPHENE COMPLEXES OF IRON *

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Summary

The mode of bonding of polymethylthiophenes has been found to depend on the source of $(\text{CpFe}^{\text{II}})^+$ used in the ligand exchange reaction. The reaction of ferrocene containing AlCl_3 and H_2O at 90°C with polymethylthiophenes gives the pure π complexes $[\text{CpFe}^{\text{II}}(\eta^5\text{-polymethylthiophene})]^+$, whereas treatment of $\text{CpFe}(\text{CO})_2\text{Cl}$ with 2,5-dimethylthiophene yields the S-bonded complex $[\text{CpFe}^{\text{II}}(\text{CO})_2(\eta^1\text{-SC}_4\text{Me}_2\text{H}_2)]^+$ (4^+). One-electron reduction of $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+$ (1^+) by LiAlH_4 gives the new air-sensitive complex $\text{CpFe}^{\text{I}}(\eta^5\text{-SC}_4\text{Me}_4)$ (**1**) which has been characterized by EPR, Mössbauer, and optical spectroscopies.

The modes of bonding of thiophene and polymethylthiophenes on transition metals are of interest because it has been suggested that $\pi(\eta^5)$ coordination of the aromatic ring of thiophene, rather than C-bonding (η^1), is involved in the catalytic hydrodesulfurization of thiophene [1]. However, S-bonded (η^1) thiophene has also been suggested as a possible intermediate [1].

π -Coordination of thiophene is known in Cr [2], Mn [3], Fe [4], and Ru [5] complexes. However, although $[\text{CpFe}(\eta^5\text{-thiophene})]^+$ is known [4], thiophene does not complex with the metal in attempted ligand exchange with ferrocene [6] or $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{solvent})_3]^2+$ ($\text{M} = \text{Rh}, \text{Ir}$) [7]. For stereoelectronic reasons, coordination of polymethylthiophenes is easier and several π -bonded complexes of tetramethylthiophene have been synthesized [7,8]. S-Coordination is less common and only three examples have been reported [9]. Those observations led us to examine

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the various modes of coordination of polymethylthiophenes to the $(\text{CpFe}^{\text{II}})^+$ moiety. We describe here the synthesis and characterization of π and S -bonded complexes of 2,5-dimethylthiophene and tetramethylthiophene with $(\text{CpFe}^{\text{II}})^+$, and also the one-electron reduction of the Fe^{II} sandwich to the Fe^{I} species.

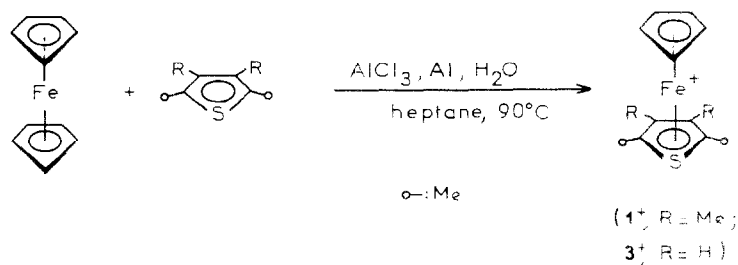
Results and discussion

Reactions of ligand exchange from ferrocene

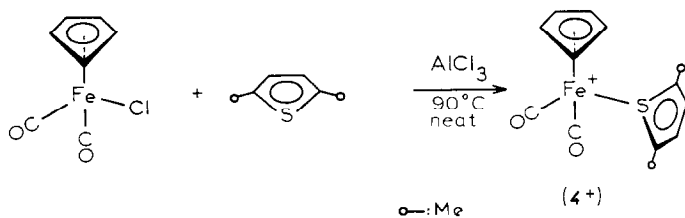
The preparation of $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^-$ (**1**⁺) by ligand exchange between ferrocene and SC_4Me_4 in the presence of AlCl_3 was described by Singer [8a] in 1976. We have found that this synthesis proceeds best at a milder temperature ($T \sim 90^\circ\text{C}$) and in the presence of 1 equiv. of H_2O (Scheme 1; these conditions prevent the demethylation of the polymethylthiophene ligand which occurs at the higher temperatures necessary for reaction in the absence of water [8c]). The cationic red complex **1**⁺ is then obtained in 50% yield by metathesis with aqueous HPF_6 . Its ^1H NMR spectrum (CD_3CN) shows two sharp singlets of equal intensity at δ 2.29 (Me_α) and 2.27 (Me_β) for the methyl groups of coordinated SC_4Me_4 . Its Mössbauer parameters (293 K): IS 0.47 mm s^{-1} vs. Fe, QS 2.12 mm s^{-1} , are consistent with a d^6 Fe^{II} structure [10,11]. The optical spectrum of **1**⁺ in CH_3CN exhibits an absorption band at λ 482 nm (ϵ 160 $\text{l mol}^{-1} \text{cm}^{-1}$), characteristic of the red colour which corresponds to the $e_2 \rightarrow a_2$ transition [11]. X-Ray crystallographic studies on **1**⁺ indicate that it crystallizes in a rhombic system ($Pnma$) with four molecules per unit cell [12].

The new cation $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^-$ (**2**⁺) is similarly obtained from 1,1'-dimethylferrocene. Complex **2**⁺ is also red, whereas the Fe^{II} sandwich complexes $[\text{CpFe}^{\text{II}}(\eta^6\text{-alkylbenzene})]^+$ are yellow; for example, the visible spectrum of $[\text{CpFe}^{\text{II}}(\eta^6\text{-C}_6\text{Me}_6)]^+ \text{PF}_6^-$ [16] shows an absorption band at λ 455 nm with a molar extinction coefficient of 66 $\text{l mol}^{-1} \text{cm}^{-1}$. These observations are consistent with the data for $[\text{CpFe}^{\text{II}}(\eta^6\text{-arene})]^+$ reported by Hendrickson [11], showing that the variation of the arene strongly perturbs the e_2 MO and not the e_1^* LUMO.

In contrast to tetramethylthiophene, π -complexation of 2,5-dimethylthiophene with the CpFe^+ moiety from ferrocene gives a low yield of the red complex $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_2\text{H}_2)]^+ \text{PF}_6^-$ (**3**⁺) (10%, Scheme 1) [8c]. Singer also reported $[(\eta^5\text{-C}_5\text{H}_4\text{Et})\text{Fe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_2\text{H}_2)]^+ \text{PF}_6^-$ [8a]. However, like $[\text{CpFe}(\eta^5\text{-thiophene})]^+$ and **1**⁺, **3**⁺ can also be made by photolysis (in the visible region) of $[\text{CpFe}(\eta^6\text{-C}_6\text{H}_5\text{Cl})]^+ \text{PF}_6^-$ and the free thiophene derivative [4] in CH_2Cl_2 .



SCHEME 1



SCHEME 2

Reaction of ligand exchange from $\text{CpFe}(\text{CO})_2\text{Cl}$

Dimethylthiophene can bind iron in a η^1 -fashion; e.g., $[\text{CpFe}(\text{NCMe})_2(\eta^1\text{-SC}_4\text{Me}_2\text{H}_2)]^+$ is known [9b]. In contrast with simple arenes [13], $\text{SC}_4\text{Me}_2\text{H}_2$ reacts with $\text{CpFe}(\text{CO})_2\text{Cl}$ to give a S -bonded complex, the thermally stable compound $[\text{CpFe}^{\text{II}}(\text{CO})_2(\eta^1\text{-SC}_4\text{Me}_2\text{H}_2)]^+ \text{PF}_6^-$ (4^+) in 21% yield (Scheme 2). The η^5 -bonded complex 3^+ is never obtained by this method, even when the reaction temperature is increased.

The infrared spectrum of 4^+ exhibits two $\nu(\text{CO})$ bands at 2060 and 2000 cm^{-1} . Its structure was confirmed by ^1H NMR spectroscopy.

Electron-transfer to 1^+

The cyclic voltammogram of $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^-$ (1^+) displays a reversible cathodic wave $\text{Fe}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{I}}$ at -1.15 V vs. the standard calomel electrode (SCE) (sweep rate: 0.1 V s^{-1} ; N,N -dimethylformamide, $n\text{-Bu}_4\text{NClO}_4$ 0.1 M , Hg cathode). The second wave $\text{Fe}^{\text{I}} \rightarrow \text{Fe}^0$ at -1.95 V vs. SCE is only slightly reversible, the 20-electron anionic complex $[\text{CpFe}^0(\eta^5\text{-SC}_4\text{Me}_4)]^-$ being unstable (Fig. 1). Such behavior is known for related $[\text{CpFe}^{\text{II}}(\eta^6\text{-arene})]^+$ complexes [14].

Na/Hg reduction of 1^+ in THF at -20°C leads to decomposition within a few seconds. It is known that Fe^{I} species are formed from their Fe^{II} cationic precursors and LiAlH_4 [15], and the new unstable deep-purple complex $\text{CpFe}^{\text{I}}(\eta^5\text{-SC}_4\text{Me}_4)$ (**1**) can be generated at -50°C by reaction of 1^+ with LiAlH_4 in THF (Scheme 3). Its EPR spectrum at 77 K in frozen THF exhibits three g values ($g_x = 2.0275$, $g_y = 2.0642$, $g_z = 1.9968$) specific for the Fe^{I} sandwich, indicating that the system is strongly distorted. The Mössbauer parameters (77 K, frozen THF) are also typical of the d^7 Fe^{I} series: IS 0.58 mm s^{-1} vs. Fe , QS 0.92 mm s^{-1} .

Although **1** is unstable as a solid, addition of an excess of cold pentane to the reaction mixture at -50°C followed by filtration gives a solution of **1** which is apparently stable at 20°C for a few hours. The visible spectrum of **1** exhibits a band at λ 537 nm (ϵ 1065 $\text{l mol}^{-1} \text{cm}^{-1}$). The colour shift from green $\text{CpFe}^{\text{I}}(\eta^6\text{-C}_6\text{Me}_6)$ (**6**) to purple (**1**) is also consistent with the fact that both complexes belong to the d^7 series [16]. The e_1^* (dxz, yz) $\rightarrow e_2$ (arene) transition responsible for the colour is more energetic for **1** because e_2 (SC_4Me_4) is higher in energy than e_2 (C_6Me_6).

It can be concluded that the complexation behavior of polymethylthiophenes towards iron is different from that of simple arenes. The present study indicates that both stable η^1 and η^5 complexes of CpFe^+ can be made, depending on the complexation reaction used. The η^5 complexes can be in several oxidation states provided the thiophene ligand is peralkylated; in particular the Fe^{I} , 19-electron d^7 compound, which is more easily destabilized than other $\text{CpFe}^{\text{I}}(\eta^6\text{-arene})$ com-

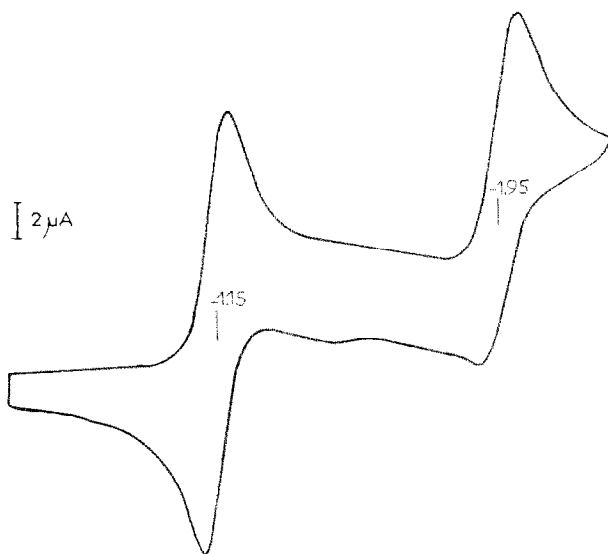
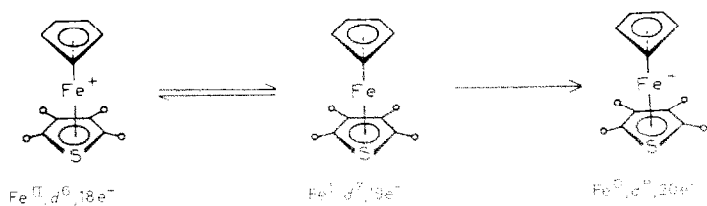
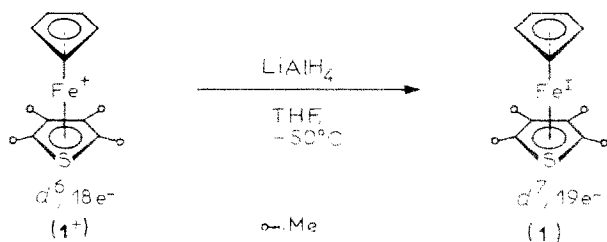


Fig. 1. Voltammogram of $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^-$ (1^+) 5.10^{-3} M in DMF, hanging Hg cathode, sweep rate: 0.1 V s^{-1} , $n\text{-Bu}_4\text{N}^+ \text{ClO}_4^-$ 0.1 M , 20°C .



SCHEME 3

pounds by THF, can be spectroscopically studied in pentane as solvent. The implication for surface chemistry and catalytic hydrodesulfurization is that two types of complexation can be envisaged: on the π complex hypothesis, surface-hydride generated from H_2 might also effect electron- rather than hydride transfer.

Experimental

General data

All manipulations were performed under N_2 or Ar by Schlenk techniques.

Reagent grade THF was predried over KOH pellets and distilled over sodium benzophenone ketyl just before use. Heptane and pentane were purified over $\text{H}_2\text{SO}_4/\text{HNO}_3$ and distilled over sodium benzophenone ketyl. Tetramethylthiophene was prepared by the published procedure [17]. All other reagents were used as received. Infrared spectra were recorded on a Pye-Unicam SP 1100 spectrometer, with samples between KBr disks in Nujol; wavenumbers are in cm^{-1} ; calibration was with polystyrene. ^1H NMR spectra were recorded with a Varian EM 360 (60 MHz) or a Bruker WP 80 (80 MHz, FT mode) spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP 80 (20,11 MHz, FT mode) spectrometer by S. Sinbandhit (Centre de Mesures Physiques de l'Ouest). All chemical shifts are reported in ppm relative to Me_4Si as internal reference. Mössbauer spectra were recorded with a 25-mCi ^{57}Co source on Rh using a symmetric triangular sweep mode, by Dr. J.-P. Mariot (Professor F. Varret's laboratory, Université du Maine). Isomer shifts (*IS*) are relative to Fe. Optical spectra were obtained on a Hitachi 100-60 spectrophotometer, with 1 cm quartz cells. The EPR spectrum was recorded with a Varian X-band spectrometer at Zurich (in Professor J.H. Ammeter's laboratory). Cyclic voltammograms were recorded on a P.A.R. 360 instrument. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne.

Preparation of $[\text{CpFe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^- (\text{I}^+)$

A mixture of ferrocene (9.3 g, 50 mmol), freshly distilled SC_4Me_4 (7 g, 50 mmol), Al powder (1.4 g, 50 mmol), AlCl_3 (20 g, 150 mmol), 0.9 ml of H_2O (50 mmol) and heptane in a 250 ml three-necked flask was stirred under N_2 and refluxed for 16 h. The mixture was then cooled to 0°C , treated with 100 ml of icewater, and filtered. The aqueous layer was separated, washed with ether (3×50 ml), then treated with aqueous NH_3 to remove Al^{3+} . The aqueous solution was then filtered, and the desired salt precipitated by addition of aqueous HPF_6 (50 mmol). The salt was dissolved in acetone, and the solution dried over MgSO_4 , filtered, and concentrated. Precipitation with an excess of ether produced 10.6 g (52% yield) of a red powder, which was shown to be pure by ^1H NMR. Recrystallization from hot ethanol gave 9 g of red needles. ^1H NMR (CD_3CN , Me_4Si) δ 4.75 (s, 5H, Cp), 2.29 (s, 6H, Me_α), 2.27 (s, 6H, Me_β). ^{13}C NMR (CD_3CN , Me_4Si) δ 102.7, 95.9 (SC_4Me_4), 79.3 (Cp), 14.0, 13.7 (SC_4Me_4). Mössbauer parameters (293 K): *IS* 0.47 mm s^{-1} vs. Fe *QS* 2.12 mm s^{-1} . UV-VIS λ (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 224 (9300), 256 (10800), 442 (176), 482 (160).

Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe}^{\text{II}}(\eta^5\text{-SC}_4\text{Me}_4)]^+ \text{PF}_6^- (\text{2}^+)$

A mixture of 1,1'-dimethylferrocene (5.1 g, 24 mmol), SC_4Me_4 (3.4 g, 24 mmol), Al powder (0.7 g, 24 mmol), AlCl_3 (9.3 g, 72 mmol), 0.5 ml of H_2O (24 mmol) and heptane (100 ml) was stirred under N_2 and refluxed overnight. Work-up as above gave 2 g (20% yield) of a powder from which 1.6 g of red microcrystals were obtained by recrystallization from hot ethanol. ^1H NMR (CD_3CN , Me_4Si) δ 4.63 (s, 4H, C_5H_4), 2.28 (s, 6H, Me_α), 2.27 (s, 6H, Me_β), 1.94 (s, 3H, CpMe). ^{13}C NMR (CD_3CN , Me_4Si) δ 102.4 (substituted C_{Cp}), 95.9, 95.7 (SC_4Me_4), 79.0, 78.9 (Cp), 13.6, 13.2 (SC_4Me_4), 12.6 (CpMe). Analysis: Found: C, 40.23; H, 4.47. $\text{C}_{14}\text{H}_{29}\text{PF}_6\text{FeS}$ calcd.: C, 40.02; H, 4.56%.

Preparation of $[\text{CpFe}^{\text{II}}(\text{CO})_2(\eta^1\text{-SC}_4\text{Me}_2\text{H}_2)]^+ \text{PF}_6^- (\mathbf{4}^-)$

A mixture of $\text{CpFe}(\text{CO})_2\text{Cl}$ (1.3 g, 6 mmol), 2,5- $\text{SC}_4\text{Me}_2\text{H}_2$ (5 ml, excess) and AlCl_3 (2.4 g, 18 mmol) under N_2 in a 100 ml three-necked flask equipped with a reflux condenser, was heated at 90°C for 16 h. After work-up (described above), 550 mg (21% yield) of a yellow powder was recovered. $^1\text{H NMR}$ (CD_3COCD_3 , Me_4Si) δ 6.60 (s, 2H, $\text{SC}_4\text{Me}_2\text{H}_2$), 5.15 (s, 15H, Cp), 2.42 (s, 6H, Me). Ir (Nujol) 2060 (s, $\nu(\text{CO})$), 2000 (s, $\nu(\text{CO})$) cm^{-1} .

Reaction of $\mathbf{1}^+$ with LiAlH_4

Optical data. THF (10 ml) at -50°C was introduced into a Schlenk tube containing cation $\mathbf{1}^+$ (406 mg, 1 mmol) and LiAlH_4 (190 mg, 5 mmol). The mixture rapidly turned deep purple. It was stirred for 15 min, then 100 ml of cold pentane were added. After filtration, 40 ml of the solution was titrated against I_2 . A 1/3 dilution allowed recording the visible spectrum. λ (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 537 (1065), 652 (252).

EPR experiment. A Schlenk tube was charged with salt $\mathbf{1}^+$ (4 mg, 0.01 mmol) and 10 ml of THF. The mixture was cooled to -80°C . LiAlH_4 (10 mg, 0.27 mmol) was added, and the solution stirred for a few minutes at -50°C . The solution was immediately transferred to an ESR tube and frozen in liquid nitrogen; EPR parameters (77 K, frozen THF): $g_x = 2.0275$, $g_y = 2.0642$, $g_z = 1.9968$.

Mössbauer experiment. THF (0.2 ml) at -80°C was introduced into a Mössbauer glass cell containing salt $\mathbf{1}^+$ (100 mg, 0.22 mmol) and LiAlH_4 (38 mg, 1 mmol), and the cell was then sealed under vacuum. The solution then allowed to warm to -50°C kept there for 15 min, then frozen in liquid nitrogen. Mössbauer parameters (77 K, frozen THF): IS 0.58 mm s^{-1} vs. Fe, QS 0.92 mm s^{-1} .

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